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Exclusive Recognition of Acetone in a Luminescent BioMOF through Multiple Hydrogen-Bonding Interactions

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Supporting Information

ABSTRACT: An anionic microporous metal-organic framework (1), featuring a combination of mononuclear and tetranuclear zinc clusters and a mix-and-match strategy of two different types of organic ligands, has been successfully constructed via a solvothermal reaction. Its luminescence can be exclusively guenched by acetone. In situ single-crystal X-ray diffraction studies reveal the specific acetone binding sites and the existence of multiple hydrogen bonds between acetone and the framework. Together with its chemical and thermal stability, 1 has been demonstrated to be a potential luminescence probe for the rapid detection of acetone with a remarkable antiinterference and a low detection limit (1.85 ppm).

cetone is a volatile chemical feedstock that has been Aextensively used in industry. Studies have shown that acetone can cause harm to the nervous systems of humans when the concentration is higher than 173 ppm.¹ On the other hand, acetone has been found in the range of 300-900 ppb in the breath of healthy people and more than 1800 ppb in those with diabetes.² Diabetic patients are required to monitor their blood glucose level, which might involve pricking for a drop of blood several times a day. This method is painful and invasive and can be unsafe. Because the concentration of breath acetone has been confirmed to be highly correlated with the blood glucose level, it is of great potential to use breath acetone as a crucial biomarker for diabetes mellitus and detect it in a pain-free and noninvasive manner. Traces of acetone can be detected by gas chromatography-mass spectrometry, selected ion flow tube mass spectrometry, etc.; however, these traditional methods are time-consuming and less desired in routine monitoring.³ Therefore, it is urgent to seek new materials that have high sensitivity and could be integrated into small, portable, and easy-to-use devices. Porous materials with the ability to absorb acetone and transform interactions into readable signals might be able to serve to this purpose.

Metal-organic frameworks (MOFs) have been emerging as very promising materials over the past few decades because of their unprecedented high surface areas, structure predictability, pore/channel tunability, etc. All of these advantages enable their potential applications in gas storage and separation, catalysis,⁵ luminescence probing,⁶ light emitting,⁷ bioimaging,⁸ and so on. As a large subset, luminescent metal-organic frameworks (LMOFs) are generally constructed with rareearth metal ions in which the metal clusters are often the origin

of luminescence. Recently, LMOFs based on nonluminescent zinc ions and luminescent organic ligands have attracted particular attention for their low expense and biocompatibility.

To date, there have been some reports on LMOFs with luminescence sensing properties toward acetone. For example, Chen et al. reported a microporous Eu-MOF exhibiting a luminescence quenching effect upon the addition of acetone, and its high selectivity was attributed to the pore size and open Eu³⁺ sites.^{13b} Zhang et al. documented the luminescence properties of two microporous Zn-MOFs, and one of them showed luminescence enhancement in the presence of acetone.¹⁰ The latter, however, failed to explain how the framework selectively interacted with acetone and enhanced its luminescence emission accordingly. In this Communication, we report a novel anionic microporous Zn-MOF, $(Me_2NH_2)_2[(Zn_8(TBAPy)_3(6-BA)_4(\mu_4-O)(H_2O)_4] (DMF)_8(H_2O)_6$ (1; DMF = N,N-dimethylformamide). Its luminescence can be exclusively quenched by acetone, and in situ single-crystal X-ray diffraction studies of the acetoneloaded 1 have revealed specific acetone binding sites inside the framework. 1 is constructed from zinc ions and two different types of ligands (Scheme S1): one is the biorelated 6benzylaminopurine (6-BA), and the other is the pyrene-based tetracarboxylate ligand 1,3,6,8-tetrakis(p-benzoic acid)pyrene (H₄TBAPy). Pyrene is a versatile luminophore with high luminescence quantum yield, which can be transformed into readable signals for viable sensing devices.¹

Single-crystal X-ray diffraction analyses revealed that 1 crystallizes in a monoclinic crystal system, with a space group of P2/c (Table S1). The asymmetric unit of 1 contains four crystallographically independent Zn²⁺ in two different coordination geometries: Zn1 and Zn2 are part of the $Zn_4O(6-BA)_4(COO)_4$ secondary building unit (SBU), each bound to N3 of one 6-BA and N9 of another 6-BA, one carboxylate O atom, and the μ_4 -O atom shared with three other Zn atoms in the SBU; Zn3 and Zn4 are both in a distorted tetrahedral geometry, each independently bound to two carboxylate O atoms of different TBAPy ligands, N7 of 6-BA, and one water molecule, forming a simple mononuclear $Zn(6-BA)(COO)_2(H_2O)$ SBU (Figures S1 and 1a). The two SBUs are bridged by 6-BA and extended into a threedimensional (3D) MOF (Figure 1b,c) by TBAPy with a calculated porosity per unit cell volume of 33.4%.¹²

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Figure 1. (a) Mononuclear and tetranuclear zinc SBUs in 1. (b) 3D structure of 1 viewed the *c* axis. (c) View of the two channels and acetone binding sites along the *b* axis. (d) Topological representation of 1 in a (3,3,4,4,8-c)-connected net with the point symbol of $\{4,6^2\}_4\{4^2,6^2,8^2\}\{4^3,6^3\}_2\{4^4,6^{18},8^6\}$.

Topological analysis of the network reveals a (3,3,4,4,8-c)connected net with the point symbol of $\{4.6^2\}_4\{4^2.6^2.8^2\}$ - $\{4^3.6^3\}_2\{4^4.6^{18}.8^6\}$ (Figures 1d and S2). 1 possesses two types of one-dimensional channels (A and B) running along the *c* axis with opening dimensions of ca. 6.4×4.2 Å and 5.5×2.8 Å, respectively (Figure 1b). In particular, channel B features an alternating pipes and cavities structure, which allows only small molecules such as acetone to go through and reach the binding sites in the cavities (Figure 1c).

The TGA curve of 1 revealed that the framework can be thermally stable up to ca. 340 °C (Figure S5). The variabletemperature powder X-ray diffraction (PXRD) was measured for 1 under a nitrogen atmosphere, indicating the framework could indeed be retained up to 340 °C (Figure S6). The finely ground samples of 1 were immersed in aqueous solutions of pH from 2 to 12 and different organic solvents for 3 days, respectively. Then the solid samples were filtered, followed by PXRD measurements. No obvious differences in the PXRD patterns were observed compared with the PXRD patterns of the as-synthesized and simulated 1 (Figures S7 and S8). These results demonstrate that both the thermal and chemical stabilities of 1 are excellent.

The luminescence properties of 1 and the two ligands in their solid states were investigated at room temperature, and their emission spectra are given in Figure S9. 1 exhibited a broad emission band centered at 486 nm upon excitation at 280 nm (Figure 2a). Interestingly, the luminescence of 1 exhibited a quantitative quenching effect when soaked in acetone but barely changed in most of the other solvents (Figure 2b). Such unusual solvent-dependent luminescence properties are of great interest for acetone sensing, which prompts us to examine it in more detail.

To study the luminescence quenching effect by acetone, 1 was first dispersed in chloroform as a standard emulsion, and then acetone was gradually added while emission was monitored. As shown in Figure 3a, the luminescence intensity



Figure 2. (a) Excitation (black dash-dotted line) and emission (red solid line) spectra of 1. (b) Histogram of the emission intensities of 1 dispersed in different organic solvents. The excitation wavelength is 280 nm.



Figure 3. (a) Emission spectra of 1 dispersed in chloroform upon the incremental addition of acetone and (b) corresponding SV plot at room temperature. (c) Regeneration cycles of 1 as a sensor for detecting acetone (red, regenerated; blue, acetone-loaded). (d) Real-time monitoring of the solid-state emission of 1 in response to acetone vapor.

of the emulsion distinctively decreased along with the addition of acetone. The curve in Figure 3b shows that the luminescence intensity at 486 nm versus the acetone concentration follows a first-order exponential decay, indicating that the luminescence quenching of 1 by acetone is diffusion-controlled.¹³ The luminescence quenching efficiency can be quantitatively expressed by the linear Stern–Volmer (SV) equation¹⁴ $I_0/I = 1 + K_{SV}[M]$, where I_0 and I are the values of the luminescence intensity of pristine 1 and acetoneloaded 1, respectively, [M] is the molar concentration of acetone, and K_{SV} is the quenching effect coefficient. The linear correlation can be fitted by $I_0/I = 1.02098 + 0.27256[M]$, with a correlation coefficient (R^2) of 0.99276 at low concentrations (<0.7 × 10⁻³ M).

Accordingly, the K_{SV} values were calculated to be 272.56 M^{-1} from the experimental data for acetone in a chloroform system. By the ratio of $3\sigma/S$ (σ is the standard deviation of 5 replicating luminescence measurements of blank solutions, and S is the slope of the calibration curve), the low detection limit is estimated to be 1.85 ppm, which is comparable to the

previously reported high-performance materials, such as Zn- PDC/Tb^{3+} , etc.¹⁵ Moreover, 1 showed excellent antiinterference in the detection of acetone. As demonstrated in Figure S11, the addition of other common organic solvents had little to none effect on acetone's quenching capability. In order to be considered in real applications, rapid response and easy regeneration are another two important indicators regarding the sensing performance. 1 can be regenerated by simply washing with DMF, and the almost complete recovery (ca. 92%; Figure 3c) of the initial luminescence intensity of 1 over five cycles implies its high regenerability and photostability. The retained PXRD pattern of 1 after five runs of measurements (Figure S12) also suggests that its framework has remained intact. The luminescence quenching efficiency of 1 upon exposure to acetone vapor was 12% in the first 2 min and 70% in 1 h, indicating that 1 can effectively detect acetone in its gas phase and could be potentially used as a real-time sensing material (Figure 3d).

According to previous reports,¹⁶ luminescence quenching by either ions or small molecules was usually caused by collapse of the framework, guest exchange, competing absorption, hostguest interaction, etc. For Zn-based LMOFs, luminescence was mostly generated from ligand-to-metal charge transfer (LMCT) and/or intraligand charge transfer $(n-\pi^* \text{ or } \pi-\pi^*)$.¹⁷ 1, 6-BA, and H₄TBAPy were first measured by their UV-vis absorption (Figure S14). The absorption spectrum of 1 features two intense and broad emission bands (250-330 and 350-460 nm), largely overlapped with the absorption spectrum of acetone (220-320 nm). Thus, the competing absorption of excitation light by acetone may weaken the energy transfer in 1, resulting in a reduced luminescence intensity. In order to gain further information for structure-property interpretation and propose a plausible mechanism for the acetone-triggered on-off luminescence switching, we managed to obtain the acetone-loaded crystals (1-acetone) in good quality for single-crystal X-ray crystallography data collection (see the Supporting Information). The locations of the acetone molecules have been revealed, and multiple hydrogen-bonding interactions between the guest acetone and host framework have been confirmed in the crystal structure of 1-acetone. As shown in Figure 4, each of the absorbed acetone molecules was locked on the surface of the framework by forming two hydrogen bonds with the H atom of the terminal water molecule and the uncoordinated carboxylate O atom, respectively. We speculate that the pipe-and-cavity structure in channel B functions as a molecular sieve, which

1 1-acetone Acetone

Figure 4. Illustration of acetone (green background) binding sites and multiple hydrogen bonds in **1-acetone**.

allows only small molecules such as acetone (molecule diameter: 4.6 Å)¹⁸ to go through and reach the binding sites in the cavities. Furthermore, the specific geometry of the cavity greatly promotes host—guest interactions with acetone by forming multiple hydrogen bonds. The incorporation of acetone in the channel rearranged the ligand orientations, and the distance between the $\pi \cdots \pi$ conjugated benzene rings of 6-BA and TBAPy expands from 3.685 to 5.642 Å. These results suggest that the exclusive luminescence quenching of 1 in the presence of acetone might be ascribed to energy transfer from pyrene ligands to acetone molecules.¹⁹

In summary, by utilizing a mix-and-match ligand strategy, we have successfully synthesized an anionic microporous MOF material with good thermal and water stability over a pH range of 2-12. Its pipe-and-cavity-alternating channel-like structure provides a molecular-sieving function, and together with its pyrene-based luminescence, 1 is an ideal platform to study host—guest recognition for small molecules. Indeed, 1 exhibits an exclusive luminescence quenching effect by acetone in solutions with a detection limit of 1.85 ppm. In situ single-crystal studies reveal multiple hydrogen bonds between the host framework and guest acetone. Moreover, 1 can also quickly recognize acetone in its gaseous phase, which renders it a potential alternative for real-time acetone monitoring in exhalation.

ASSOCIATED CONTENT

S Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.inorg-chem.9b00873.

Experimental section, crystallographic data, characterizations, and photophysical measurements (PDF)

Accession Codes

CCDC 1903651 and 1903652 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/data_request/cif, or by emailing data_request@ccdc.cam.ac.uk, or by contacting The Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: +44 1223 336033.

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The manuscript was written through contributions of all authors. All authors have given approval to the final version of the manuscript.

Notes

The authors declare no competing financial interest.

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